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(54) **HYDROPHILIC WORKING METHOD FOR SURFACE OF MOLDING**

(57)Abstract:

PURPOSE: To provide the novel hydrophilic photocontrol method which introduces a hydrophilic group selected in concn. in compliance with a design into the surface of a molding according to its position.

CONSTITUTION: The hydrophilic group is introduced into the surface of the molding having a photodimerization reactive photosensitive group by irradiating this surface with light, such as visible light or UV light, in the vapor of a photosensitive treating agent for hydrophilicity impartation having the same photosensitive group as the above-mentioned photosensitive group. The hydrophilicity photocontrol of a high degree which is by far hardest to be attained by the conventional technology is executed in this way and this method is applicable to the controlled hydrophilic working of moldings, such as electronic circuit materials, master plates for offset printing, packaging films, clothing, and biomaterials.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the hydrophilic processing method for the front face of Plastic solids, such as a textile, a film, a poly membrane, and electronic material, and the method of controlling the hydrophilic property on the front face of a Plastic solid by light by introducing a hydrophilic radical into the optical irradiation portion of the front face which has a photosensitive machine using the photoreaction of a photosensitive machine in more detail.

[0002]

[Description of the Prior Art] Although various methods are developed, the hydrophilic processing method which hydrophilicity-izes the front face of a Plastic solid which consists of various materials, such as a metal, ceramics, and a macromolecule, serves as many products and it is put in practical use conventionally, the method of hydrophilicity-izing attracts attention as a new processing method by irradiating a Plastic-solid front face, forming the hydrophilic matter in the front face by the energy, or covering light, such as ultraviolet rays and a visible ray, above all. That is, this method can hydrophilicity-ize alternatively only the portion which irradiated light, and since the grade of hydrophilicity-izing can moreover be adjusted with the quantity of light (luminous-intensity x irradiation time), it accepts as what can be applied to various uses.

[0003] In addition, the hydrophilic property said here means that hydrophilicity-ization gives the above-mentioned hydrophilic property for the property of expressing compatibility with water, such as wettability to water, hygroscopicity over a steam, and moisture permeability, again.

[0004] The method of irradiating ultraviolet radiation and hydrophilicity-izing it in oxygen or air, to hydrophobic macromolecules, such as a polyethylene terephthalate, as a method of controlling a surface hydrophilic property by such light, is learned. Although the surface hydrophilic property was easily improvable according to this method, there were prolonged being irradiated and a problem referred to as that a front face will carry out hydrophobing again if time passes after irradiation.

[0005] As a method of solving such a trouble, the method of carrying out the optical graft polymerization of the hydrophilic monomer to a hydrophobic macromolecule is learned. This method is performed by flooding a hydrophobic film with the solution of hydrophilic monomers, such as a sensitizer or an optical radical initiator, and an acrylic acid, and irradiating light. Although it has the advantage said that hydrophilicity-izing of a hydrophobic film is possible and the endurance of the hydrophilicity-ized front face is also good according to this method, since the monomer described above in the solution carried out a polymerization, a homopolymer generated and it was hard to remove this by the generated radical, prolonged extraction needed to be performed using the solvent into which only this homopolymer melts. It was difficult for the radical moreover generated to start a chain transfer in places other than the optical irradiation section on a Plastic-solid front face, and for a radical polymerization to happen from the place, and to hydrophilicity-ize only an optical irradiation portion.

[0006] In order to improve such a fault, the method (journal OBU polymer science : a polymer letter edition, 20 s 17-21 page 1982) of carrying out the graft polymerization of the hydrophilic monomer to a high polymer film by the gaseous phase is studied. Although it was possible to have introduced a hydrophilic group into a specific position, photopolymerization initiators, such as a sensitizer and an optical radical generating agent, were required like the graft polymerization in a liquid phase system, and complicated operation of making it swelling a processed material with a solvent beforehand to blend with a Plastic-solid front face the additive which governs such a reaction, or infiltrating an additive into it was required of this method. Moreover, in order that the moisture of the minute amount contained in a processed material might affect this reaction greatly, attachment of a facility special to moisture control of dryness of a processed material, a processing gas, and atmosphere and quality control-consideration needed to be performed.

[0007] It such a fault not only causes the problem of the complicated nature on a processing process, and a raise in cost, but brings about the fall also with a remarkable precision of a hydrophilic optical controllability. That is, although the fixed degree of hydrophilicity can be maintained if all of these factors are not controlled strictly since factors, such as temperature of not only the quantity of light but a sensitizer, a photopolymerization initiator, moisture, the degree of swelling on the front face of a Plastic solid, evaporation graft agent concentration, a Plastic-solid front face, and a gas graft agent, keep functionality complicated as a factor which governs the degree of hydrophilicity of a processed material and it is involving, in an actual Plastic solid, such management is the most difficult. In the case of the matter which has an uneven surface detailed organization like especially a macromolecule Plastic solid, the inclination is strong. Furthermore, the homopolymer generated this method like the graft polymerization in a liquid phase system, and it had the problem that removal of this took a long time and a great effort.

[0008]

[Problem(s) to be Solved by the Invention] this invention was performed in view of this present condition, and solves the trouble which the hydrophilic light controlling method in the Plastic-solid front face of these former has, and it aims at offering the new hydrophilic processing method which is easier operation, and controls a hydrophilic property according to the surface position of a Plastic solid with advanced repeatability, without pretreating addition of optical system-of-reaction additives, such as an initiator and a sensitizer, and the Plastic-solid front face accompanying it.

[0009]

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, on the Plastic-solid front face which has the photosensitive machine of photodimerization nature In the steam of the organic compound which comes to have this photosensitive machine, the photosensitive machine with which photodimerization nature can be caused, and at least one hydrophilic radical Irradiate an ultraviolet beam of light and/or a visible ray, and the photosensitive machine on this front face of a Plastic solid and the photosensitive machine of this organic compound are made to react. By adopting the hydrophilic processing method on the front face of a Plastic solid characterized by introducing a hydrophilic radical into an optical irradiation portion, and changing a surface hydrophilic property, it found out attaining the above-mentioned purpose and this invention was reached.

[0010] The work of various configurations, such as the paper and fiber which consist of a composite of various materials, such as a metal, a stone, carbon material, glass, ceramics, wood, leather, and a synthetic macromolecule, or these materials as a Plastic solid set as the object of hydrophilic processing in this invention, a textile, the foil, a film, a film, a sheet, a board, and a molding workpiece, can be used.

[0011] Anythings can be used for it if the photosensitive machine which can be used by this invention has photodimerization nature. If these is enumerated, there are annular unsaturation conjugate carbonyl compound residues, such as unsaturation conjugate carbonyl compound residues, such as cinnamoyl machines which form a cyclobutane ring by optical irradiation, chalcone residues, and thinner millimeter DIN machines, a coumarin residue, a pyrone residue, a thymine residue, and maleimide residues, and anthryl machines to which a bridging happens by the ring comrade. That to which it dimerizes and disassembly of a photosensitive machine etc. cannot take place easily in the process of evaporation and sublimation mentioned later in this due to the light of a near-ultraviolet shell visible region is desirable. Even if there is photodimerization nature, since things which have absorption in the ultraviolet region of short wavelength, such as olefins, may concur with decomposition etc. by optical irradiation, they are not so desirable.

[0012] The introductory method of the photosensitive machine on the front face of a Plastic solid used by this invention chooses the most suitable thing according to the material of the target Plastic solid. For example, in the case of the material of inorganic systems, such as a metal, a stone, glass, and ceramics, the reaction of organosilane compounds, such as aminopropyl triethoxysilane, 3-chloropropyl trichlorosilane, and 3-isocyanate propyl triethoxysilane, and a Plastic solid can be used, reactant functional groups, such as an amino group, a halogen machine, and an isocyanato group, can be introduced into it, and it can introduce into it at a well-known reaction using this.

[0013] It can introduce further again using the organosilane compound expressed with general formula $R-X-Si(CH_3)_n Z_3-n$ (however, the compound machine with which R in a formula has a photosensitive machine and both X has an alkylene machine, an arylene machine, or both bases, and Z express a halogen machine and an alkoxy group, and n is 0, 1, and 2). The alkylene machine may include branching units, such as joint machines, such as ether linkage, amide combination, ester combination, ketone combination, and sulfone combination, and an alkyl group, etc. inside, and is not limited to polymethylene combination at all. It is desirable that they are the chloro machine with comparatively easy composition as a halogen machine, a methoxy machine from a reactant point with the Plastic solid later mentioned as an alkoxy group, or an ethoxy basis. Although the introductory method of a photosensitive machine was indicated here, the method that otherwise it is well-known cannot be used for it, and it is not necessarily limited to this method in any way.

[0014] In this processing, since the moisture which is sticking to a Plastic-solid front face may check the reaction of the organosilane compound mentioned above and the active hydrogen on the front face of a Plastic solid or may serve as hindrance over introduction of a photosensitive machine, as for a Plastic solid, fully drying is desirable. In addition, it is better to avoid what dissolves the target Plastic solid as a solvent used in case a photosensitive machine is introduced, or is swollen.

[0015] Although that to which a Plastic solid has the organosilane compound described above on the front face at least and active hydrogen with reactivity in the case of organic system materials, such as a synthetic macromolecule, wood, paper, and leather, can introduce a photosensitive machine into the front face by the aforementioned method, when there is nothing as if, it is necessary to perform this with another chemical means. In such a case, the method of combining chemically with the active spot the graft unit which formed the active spot of a radical, active hydrogen, etc. in the molecule principal chain or the side chain, for example by (1) macromolecule reaction, and contained this photosensitive machine by the graft reacting method or the graft polymerization method. (2) It is the method of considering as the Plastic solid which copolymerizes the monomeric unit containing this photosensitive machine with a polymerization or other monomeric units, compounds the macromolecule which has many photosensitive machines, fabricates this, and makes this macromolecule the main construct, or coating the coating liquid which makes this synthetic macromolecule a principal component on Plastic-solid front face where this is another. (3) How to introduce this photosensitive machine by compounding the macromolecule which has a reactant machine by methods, such as a copolymerization method, making a photosensitive machine content processing agent with both the sensitive machine which has reactivity to this reactant machine in this, and this photosensitive machine act, and combining a reactant machine and a sensitive machine. (4) It has the sensitive machine of a large number which have reactivity to the reactant machine with both this photosensitive machine and a reactant machine of a photosensitive machine content processing agent, support coating of the

Plastic-solid front face is carried out by the strong primer (oligomer or polymer) of a Plastic-solid front face and compatibility, and methods, such as the method of making the above-mentioned photosensitive machine content processing agent act on this, combining a reactant machine and a sensitive machine, and introducing this photosensitive machine, can apply suitably.

[0016] In each above example, although a reactant machine and a sensitive machine are bases which make a pair mutually and react, the thing which carries out ionic bond not only according to what carries out a chemical bond according to covalent bond but according to an ion pair, or the thing which forms and carries out the chelate bond of the complex is included.

[0017] The organic compound which comes to have the photosensitive machine and at least one hydrophilic radical which can be combined by the photosensitive machine and photodimerization on the front face of a Plastic solid which can be used for this invention (henceforth) a light-sensitive nature hydrophilicity-ized processing agent -- calling -- general formula $R-X-Y_n$ The compound machine with which it is the compound expressed, and R in a formula has a photosensitive machine and both X has an alkylene machine, an arylene machine, or both bases, and Y_n n hydrophilic radicals (n expresses one or more integers) are expressed. The photosensitive machine said here is the same as the photosensitive machine on said Plastic solid. Furthermore, the alkylene machine said here is not necessarily limited to polymethylene combination in any way, and may include branching units, such as joint machines, such as ether linkage, ester combination, amide combination, ketone combination, and sulfone combination, and an alkyl group, etc.

[0018] As a hydrophilic radical, polar groups, such as the amino group, the 4th class ammonium, a hydroxyl, a carboxylic-acid machine, a carboxylic-acid amide group, a sulfonic acid group, and a sulfamide machine, are desirable.

[0019] Since the light-sensitive nature hydrophilicity-ized processing agent of this invention is made to evaporate or sublimate and is made to react in the state of a gaseous phase, what is easy to carry out remarkable evaporation under reduced pressure at least is still more desirable. In addition, what decomposes by evaporation, sublimation, and optical irradiation, causes the side reaction and transformation of transition etc., or separates is not desirable.

[0020] In order to make said light-sensitive nature hydrophilicity-ized processing agent react with the photosensitive machine on the front face of a Plastic solid and to introduce a hydrophilic radical on a Plastic solid, the vacuum evaporation equipment incorporating optical system which is illustrated to drawing 1 can be used. Drawing 1 is the schematic diagram of the equipment in the treatment process shown as an example of the embodiment of this invention, and the operation information serves as a procedure as shown below.

[0021] The light-sensitive nature hydrophilicity-ized processing agent 3 is put in in a boat 2, after installing Plastic solid 1 into which it comes chemically to introduce the photosensitive machine which has photodimerization nature on the front face in the upper part, a cock 9 is opened and the inside of a bell jar 8 is made into a vacuum with a vacuum pump 5. As for the degree of vacuum at this time, it is desirable that they are 10 to 2 or less Torrs. Since a peroxide may be formed and formation of a thin film may be checked in case it is the optical irradiation which will be later mentioned if oxygen remains in the bell jar, once inactive gas replaces the inside of a bell jar to photoreaction, such as nitrogen gas, it is desirable to make it a vacuum again. Since a light-sensitive nature hydrophilicity-ized processing agent cannot evaporate easily unless a degree of vacuum is still more enough, it is not desirable. If a heater 4 is heated, a light-sensitive nature hydrophilicity-ized processing agent will be evaporated or sublimated gradually, and the steam will be filled with it in a bell jar. But when this processing agent sublimates at a room temperature, it is not necessary to heat.

[0022] Thus, if an ultraviolet beam of light and/or a visible ray are irradiated from the light source 6 through an aperture 7 at a Plastic solid after making a Plastic solid exist in the steam of a light-sensitive nature hydrophilicity-ized processing agent, a hydrophilic radical is introduced in response to the optical irradiation side of a Plastic solid, and the photosensitive machine of a light-sensitive nature hydrophilicity-ized processing agent and the photosensitive machine on the front face of a Plastic solid can make a surface hydrophilic property change. The aperture used by this invention needs to be formed with the quality of the material which penetrates the light of wavelength required for the photoreaction. Moreover, between this aperture and the light source, a condenser lens 10 and light filter 11 grade can be arranged suitably.

[0023] this invention can describe the figure by which the pattern formation which consists of a part for a hydrophilic part and a canal portion, or the shade pattern of various hydrophilic properties was drawn on the Plastic solid by irradiating light or scanning a light beam, after putting a mask suitable on the Plastic-solid front face which introduced this photosensitive machine again, or the shading screen of the various degrees of shading. The concentration, therefore the degree of hydrophilic property of about 1 yuan of the hydrophilic group introduced by the method of the invention in this application are controllable by the product of luminous intensity and irradiation time-like, as described the quantity of light of the irradiation light on the front face of a Plastic solid, i.e., before. Therefore, as compared with the system [as / in the conventional optical graft method] in which many factors participate intricately and are governing the hydrophilic property, this method is excellent in controllability ability much more, and can describe patterns, such as a hydrophilic-canal pattern with very sufficient repeatability, and a hydrophilic shade figure. Hereafter, the example of reference, an example, and the example of comparison explain this invention in more detail.

[0024]

[Example]

Example of reference After putting in and carrying out the deaeration sealed tube of the 0.1ml of the 10wt% isopropyl alcohol solutions of 9-allyl-compound anthracene 2.2g, dimethyl chlorosilane 1.9g, and a chloroplatinic acid and 6 hydrate into the 1 (introduction of photosensitive machine to inorganic system Plastic-solid front face) glass sealed tube, it heated at 100 degrees C for 6 hours. After opening, the solid-state which condensed reaction mixture and deposited was recrystallized from the hexane, and 9-anthryl propyl chloro dimethylsilane 2.4g was obtained. Furthermore, in the 1cmx2cm size which gave washing and

dryness beforehand to the 1wt% toluene solution of obtained 9-anthryl propyl chloro dimethylsilane, after the quartz board with a thickness of 4mm was immersed for 1 minute, it pulled up, and it heat-treated at 70 degrees C for 1 hour, and the Plastic solid which the anthryl machine combined on the front face was obtained. It checked having combined the anthryl machine from visible-ultraviolet-absorption-spectrum measurement of a Plastic solid. It was 90 degrees when the contact angle to water was measured.

[0025] example of reference as 1-(2-anthryl) ethyl methacrylate 0.2g compounded according to the method (MAKUROMO liqueur eight s 8 pages - 9-page 1975) of 2 (introduction of photosensitive machine to organic system Plastic-solid front face) SHUTORUKA, styrene 5.8g, and a radical polymerization initiator -- azobisisobutyronitril 0.04g -- benzene 60ml -- after dissolving and carrying out the deaeration sealed tube to inside, the polymerization was performed at 60 degrees C for 12 hours, and the polymer of number average molecular weight 100,000 was obtained Melting fabrication of this polymer was carried out, and the tabular Plastic solid of 2cm angle was obtained by 5mm in thickness. It checked that the anthryl machine had combined with the base on this Plastic-solid front face from ultraviolet-visible-absorption-spectrum measurement. It was 88 degrees when the contact angle to water was measured about this sample.

[0026] Example of comparison After taking a 1g anthracene on a boat, installing up the Plastic solid prepared in the example 1 of reference with the equipment of 1 view 1 and nitrogen gas's replacing the inside of a bell jar, the degree of vacuum of 10-4Torr was made to reach with a vacuum pump. Heating a boat at 150 degrees C and making an anthracene sublimate, by using a 1kW mercury lamp as the light source, it let L-39 by Toshiba Corp. filter pass, and optical irradiation of the light of long wavelength was carried out for 1 minute from 380nm at the aforementioned Plastic solid. When the ultraviolet-visible absorption spectrum of the Plastic solid after irradiation was measured, absorption (this absorption is called henceforth) of an anthryl machine disappeared, and it was confirmed that the anthryl machine on the front face of a Plastic solid and the sublimated anthracene have reacted. When the contact angle to water was measured, it was hardly as changeful as irradiation before at 89 degrees.

[0027] Example of comparison Except having put nothing into two boats, it was made completely the same as the example 1 of comparison, and light was irradiated. When the absorption spectrum of the Plastic solid after irradiation was measured, change was hardly accepted in absorption. When the contact angle to the water of the Plastic solid after irradiation was measured, it is 90 degrees and did not change irradiation before.

[0028] Example of comparison Except having used the Plastic solid prepared in the example 2 of 3 reference, it was made completely the same as the example 1 of comparison, and light was irradiated. When the ultraviolet-visible absorption spectrum of this irradiated Plastic solid was measured, this absorption decreased and it was confirmed that the anthryl machine on the front face of a Plastic solid and the sublimated anthracene have reacted. It turns out that the value of 86 degrees is acquired when the contact angle to the water of this irradiated Plastic solid is measured, and it is hardly changing irradiation before.

[0029] Example of comparison Except having used the Plastic solid prepared in the example 2 of 4 reference, it was made completely the same as the example 2 of comparison, and light was irradiated. When the ultraviolet-visible absorption spectrum of this irradiated Plastic solid was measured, change was hardly accepted in absorption.

[0030] Example 1g of 3-(9-anthryl) propionic acids was taken on one boat, and light was irradiated on the same conditions as the example 1 of comparison except having made heating temperature into 190 degrees C. It was confirmed that these absorption spectrums of the Plastic solid after irradiation decreased in number, the reaction occurred, and the carboxyl group was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 60 degrees and the hydrophilic property was changing.

[0031] Example 1g of 9-anthracene carboxylic acids was taken on two boats, and light was irradiated on the same conditions as the example 1 of comparison except having made heating temperature into 200 degrees C. It was confirmed that these absorption spectrums of the Plastic solid after irradiation decreased in number, the reaction occurred, and the carboxyl group was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 65 degrees and the hydrophilic property was changing.

[0032] Example 9-anthracene methano-RU 1g was taken on three boats, and light was irradiated on the same conditions as the example 1 of comparison except having made heating temperature into 160 degrees C. It was confirmed that these absorption spectrums of the Plastic solid after irradiation decreased in number, the reaction occurred, and the hydroxyl was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 75 degrees and the hydrophilic property was changing.

[0033] Example 3-(9-anthryl) propylamine 1g was taken on four boats, and light was irradiated on the same conditions as the example 1 of comparison except having made heating temperature into 180 degrees C. It was confirmed that these absorption spectrums of the Plastic solid after irradiation decreased in number, the reaction occurred, and the amino group was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 55 degrees and the hydrophilic property was changing.

[0034] Example Except having used the Plastic solid prepared in the example 2 of 5 reference, it was made completely the same as an example 1, and light was irradiated. When the ultraviolet-visible absorption spectrum of this irradiated Plastic solid was measured, this absorption was decreasing and absorption of a carboxyl group was newly accepted. Therefore, it was confirmed that this reaction occurred and the carboxyl group was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 65 degrees and the hydrophilic property was changing.

[0035] Example Except having used the Plastic solid prepared in the example 2 of 6 reference, it was made completely the same as an example 4, and light was irradiated. When the ultraviolet-visible absorption spectrum of this irradiated Plastic solid was

measured, this absorption was decreasing and absorption of the amino group was newly accepted. Therefore, it was confirmed that this reaction occurred and the amino group was introduced. When the contact angle to the water of the Plastic solid after irradiation was measured, the contact angle decreased at 60 degrees and the hydrophilic property was changing.

[0036]

[Effect of the Invention] Without blending and adding photoreaction system additives, such as a sensitizer and a photopolymerization initiator, according to this invention explained above Since a hydrophilic radical can be introduced into the specific position on the various front faces of a Plastic solid with sufficient repeatability according to an easy process or the shade pattern of a hydrophilic property can be formed The hydrophilic advanced light control which could not reach with the conventional technology is attained. Production of the master version in adhesive improvement; offset printing of the various substrates used with electronic material; An artificial bone, improvement [of the biocompatibility on front faces of biomedical materials, such as an artificial blood vessel,]; -- the object for packing which carried out the special design of printing nature and the gas permeability -- it can be used suitable for various uses, such as an amenity clothing; amphoteric-electrolyte type poly membrane which adjusts film; moisture permeation and sweat water absorption with a sufficient degree

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CLAIMS

[Claim(s)]

[Claim 1] The hydrophilic processing method on the front face of a Plastic solid characterized by irradiating an ultraviolet beam of light and/or a visible ray, making the photosensitive machine on this front face of a Plastic solid, and the photosensitive machine of this organic compound react, and introducing a hydrophilic radical on the Plastic-solid front face which has the photosensitive machine of photodimerization nature at the optical irradiation portion in the steam of the organic compound which comes to have this photosensitive machine, the photosensitive machine with which photodimerization can be caused, and at least one hydrophilic radical.

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(54)【発明の名称】 成形体表面の親水加工法

(57)【要約】

【目的】 成形体表面にその位置に応じてデザイン通りに濃度の選択された親水性基を導入する新規な親水性の光制御法を提供する。

【構成】 光二量化反応性の感光性基を有する成形体の表面に、これと同じ感光性基を持つ光感应性親水化処理剤の蒸気中で、可視光、紫外光等の光を照射することによって、親水性基を導入する。

【効果】 本発明の方法を用いれば、従来技術にては到達し得なかった高度の親水性光制御が可能となり、電子回路材料、オフセット印刷のマスター版、包装フィルム、衣料品、生体材料等の成形体の制御された親水加工に利用できる。

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【特許請求の範囲】

【請求項1】 光二量化反応性の感光性基を有する成形体表面に、該感光性基と光二量化反応を惹起し得る感光性基と少なくとも1個の親水性基を有してなる有機化合物の蒸気中で、紫外光線及び／又は可視光線を照射し、該成形体表面の感光性基と該有機化合物の感光性基を反応させて、その光照射部分に親水性基を導入することを特徴とする成形体表面の親水加工法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、布帛、フィルム、高分子膜、電子材料等の成形体の表面に対する親水加工法、さらに詳しくは、感光性基の光反応を利用して感光性基を有する表面の光照射部分に親水性基を導入することにより成形体表面の親水性を光によって制御する方法に関するものである。

【0002】

【従来の技術】従来、金属、セラミックス、高分子等各種素材よりなる成形体の表面を親水化する親水加工法は種々の方法が開発され数々の製品となって実用化されているが、なかんずく、紫外線、可視光線等の光を成形体表面に照射して、そのエネルギーにより親水性物質をその表面に形成したり被覆することにより親水化する方法は新しい加工法として注目を集めている。すなわち、本法は光を照射した部分のみ選択的に親水化することが可能で、しかもその光量（光度×照射時間）によって親水化の程度を調節することができるので、多様な用途に適用し得るものと認められている。

【0003】なお、ここに言う親水性とは水に対する濡れ性、水蒸気に対する吸湿性、透湿性等の水との親和性を表す特性を、又親水化とは上記親水性を付与することを意味している。

【0004】このような光によって表面の親水性を制御する方法としては、ポリエチレンテレフタレート等の疎水性高分子に酸素中あるいは空気中で紫外光を照射して親水化する方法が知られている。この方法によれば簡単に表面の親水性を改良できるが、長時間の照射が必要であることや、照射後に時間が経過すると表面が再び疎水化してくるという問題があった。

【0005】このような問題点を解決する方法として、疎水性高分子に親水性モノマーを光グラフト重合する方法が知られている。この方法は、増感剤あるいは光ラジカル開始剤とアクリル酸等の親水性モノマーの溶液に疎水性フィルムを浸漬して光を照射することによって行なわれる。この方法によれば疎水性フィルムの親水化が可能であり親水化された表面の耐久性もよいと言う利点を有しているものの、発生したラジカルによって溶液中で前記したモノマーが重合しホモポリマーが生成してしまい、これが除去し難いためにこのホモポリマーのみが溶ける溶媒を用いて長時間の抽出を行う必要があった。そ

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うえ発生したラジカルが成形体表面上の光照射部以外の場所に連鎖移動を起こしその場所からラジカル重合が起こったりすることがあり、光照射部分だけを親水化するということが困難であった。

【0006】このような欠点を改良するために気相で高分子フィルムに親水性モノマーをグラフト重合する方法（ジャーナル・オブ・ポリマーサイエンス：ポリマーレター・エディション、20巻 17～21頁 1982年）が研究されている。この方法では、特定の位置に親水基を導入することが可能であるものの、液相系でのグラフト重合と同様に増感剤や光ラジカル発生剤等の光重合開始剤が必要であり、このような反応を支配する添加剤を成形体表面に配合するには予め被処理物を溶媒で膨潤させておいたり、それに添加剤を含浸させたりする煩雑な操作が必要であった。また被処理物中に含まれる微量の水分が本反応に大きく影響を及ぼすために被処理物の乾燥と処理気体及び雰囲気の水成分コントロールに特別の設備の付設と品質管理的配慮を行う必要があった。

【0007】このような欠点は単に加工プロセス上の煩雑性、高コスト化という問題を惹起するだけではなくて親水性の光制御性の精度も著しい低下をもたらすものである。すなわち、被処理物の親水度を支配するファクターとして光量だけではなく、増感剤、光重合開始剤、水分、成形体表面の膨潤度、気化グラフト剤濃度、成形体表面及び気体グラフト剤の温度等の因子が複雑に相関性を保って関与しているので、これらの因子をすべて厳密に制御しないと一定の親水度が保てないことになるが、現実の成形体においてはこのような管理は至難のことである。特に高分子成形体のように不均一な表面微細組織を有する物質の場合はその傾向が強い。さらに本法は液相系でのグラフト重合と同様にホモポリマーが生成してしまい、これの除去に長時間と多大の労力を要するという問題があった。

【0008】

【発明が解決しようとする課題】本発明はかかる現状に鑑みて行われたもので、これら従来の成形体表面における親水性光制御法のもつ問題点を解決し、より簡単な操作で、かつ開始剤や増感剤等の光反応系添加剤の添加、及びそれに伴う成形体表面の前処理を行うことなく、高度の再現性をもって成形体の表面位置に応じ親水性を制御する新規な親水加工法を提供することを目的とするものである。

【0009】

【課題を解決する手段】本発明者らは、上記課題を解決するために鋭意研究した結果、光二量化反応性の感光性基を有する成形体表面に、該感光性基と光二量化反応性を惹起し得る感光性基と少なくとも1個の親水性基を有してなる有機化合物の蒸気中で、紫外光線及び／又は可視光線を照射し、該成形体表面の感光性基と該有機化合物の感光性基を反応させて、光照射部分に親水性基を導入

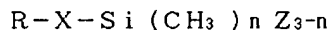
入し表面の親水性を変えることを特徴とする成形体表面の親水加工法を採用することにより、上記目的を達成することを見出し、本発明に到達した。

【0010】本発明にて、親水加工の対象となる成形体としては金属、石材、炭素材、ガラス、セラミックス、木材、皮革、合成高分子等の各種素材、あるいはこれら素材の複合材からなる、紙、繊維、布帛、フィルム、膜、フィルム、シート、ボード、成型加工品等の各種形状の加工物が使用できる。

【0011】本発明で、用いることの出来る感光性基は、光二量化反応性があればいかなるものでも用いることが出来る。これを列挙すれば、光照射によってシクロブタン環を形成するシンナモイル基類、カルコン残基類、シンナミリデン基類等の不飽和共役カルボニル化合物残基類、クマリン残基、ピロン残基、チミン残基、マレイミド残基類等の環状不飽和共役カルボニル化合物残基類、芳香環同志で橋かけの起こるアンスリル基類等がある。この中でも、近紫外から可視域の光によって二量化し、後述する蒸発・昇華の過程においても感光性基の分解等が起りにくいものが好ましい。光二量化反応性があってもオレフィン類等の、あまり短波長の紫外域に吸収を持つものは光照射によって分解等を併発することがあるので好ましくない。

【0012】本発明で用いられる、成形体表面への感光性基の導入方法は、対象とする成形体の素材に応じて最も適切なものを選択する。例えば、金属、石材、ガラス、セラミックス等の無機系の素材の場合には、アミノプロピルトリエトキシシラン、3-クロロプロピルトリエトキシシラン、3-イソシアナートプロピルトリエトキシシラン等のオルガノシラン化合物と成形体との反応を利用してアミノ基、ハロゲン基、イソシアナート基等の反応性の官能基を導入し、これを利用して公知の反応で導入することが出来る。

【0013】さらに又、一般式



(ただし、式中のRは感光性基、Xはアルキレン基、アリーレン基あるいは両基を共に有する複合基、Zはハロゲン基、アルコキシ基を表し、nは0、1、2である)で表わされるオルガノシラン化合物を用いて導入できる。アルキレン基は内部にエーテル結合、アミド結合、エステル結合、ケトン結合、スルホン結合等の結合基やアルキル基等の分岐単位等を含んでいてもよく、なんらポリメチレン結合に限定されるものではない。ハロゲン基としては比較的合成の容易なクロロ基、アルコキシ基としては後述する成形体との反応性の点からメトキシ基あるいはエトキシ基であることが好ましい。感光性基の導入方法は、ここに記載されたものの他に公知の方法を利用することができ、何等この方法に限定されるわけではない。

【0014】本処理において、成形体表面に吸着してい

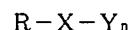
る水分は、前述したオルガノシラン化合物と成形体表面の活性水素との反応を阻害したり、感光性基の導入に対しての妨げとなったりすることがあるので、成形体は十分に乾燥しておくのが好ましい。なお、感光性基を導入する際に用いられる溶媒としては対象とする成形体を溶解したり膨潤するものは避けた方がよい。

【0015】成形体が合成高分子、木材、紙、皮革、等の有機系素材の場合には、少なくともその表面に前記したオルガノシラン化合物と反応性のある活性水素を持つものは前記方法にて感光性基をその表面に導入することができるが、さもないときは別の化学的手段にてこれを行う必要がある。このような場合には、例えば(1)高分子反応によって分子主鎖又は側鎖にラジカル、活性水素等の活性点を形成し、グラフト反応法又はグラフト重合法によって本感光性基を含んだグラフト単位をその活性点に化学的に結合する方法。(2)本感光性基を含んだモノマー単位を重合あるいは他のモノマー単位と共重合して、多数の感光性基を有する高分子を合成し、これを成形して本高分子を主構成体とする成形体とするか、あるいはこれとは別の成形体表面にこの合成高分子を主成分とするコーティング液をコーティングする方法。

(3)共重合法等の方法により反応性基を有する高分子を合成し、これに本反応性基に対して反応性を有する感応性基と本感光性基とを共に持った感光性基含有処理剤を作用させて反応性基と感応性基とを結合させることにより本感光性基を導入する方法。(4)本感光性基と反応性基とを共に持つ感光性基含有処理剤の反応性基に対して反応性を有する多数の感応性基を持ち、成形体表面と親和性の強いプライマー(オリゴマー又はポリマー)によって成形体表面をアンカーコーティングしておき、これに上記感光性基含有処理剤を作用させて反応性基と感応性基を結合し本感光性基を導入する方法、等の方法が好適に適用することができる。

【0016】以上の各例において、反応性基及び感応性基は互いに対をなして反応する基であるが、共有結合によって化学結合するものだけでなく、イオン対によってイオン結合するもの、あるいは錯体を形成しキレート結合するものを含んでいる。

【0017】本発明に用いることの出来る成形体表面の感光性基と光二量化反応によって結合し得る感光性基と少なくとも1個の親水性基を有してなる有機化合物(以後、光感応性親水処理剤と称する)は、一般式



で表わされる化合物であり、式中のRは感光性基、Xはアルキレン基、アリーレン基、あるいは両基を共に有する複合基、 Y_n はn個(nは1以上の整数を表す)の親水性基を表す。ここで言う感光性基は、前記した成形体上の感光性基と同じものである。さらに、ここで言う、アルキレン基は、なんらポリメチレン結合に限定されるわけではなく、エーテル結合、エステル結合、アミド結

合、ケトン結合、スルホン結合等の結合基やアルキル基等の分岐単位等を含んでいてもよい。

【0018】親水性基としては、アミノ基、第4級アンモニウム基、ヒドロキシル基、カルボン酸基、カルボン酸アミド基、スルホン酸基、スルファミド基等の極性基が好ましい。

【0019】さらに本発明の光感応性親水化処理剤は、蒸発又は昇華させて気相状態にて反応させるので、少なくとも減圧下にてかなり気化しやすいものが好ましい。なお蒸発、昇華、光照射によって分解したり、転移等の副反応・変質を起こしたり、遊離したりするものは好ましくない。

【0020】前記した光感応性親水化処理剤を成形体表面の感光性基と反応させ、成形体上に親水性基を導入するには、図1に例示するような光学系を組み込んだ蒸着装置を用いることが出来る。図1は本発明の実施態様の一例として示した処理プロセス中の装置の概略図であって、その操作法は以下に示したような手順となる。

【0021】光感応性親水化処理剤3をボート2内に入れ、その表面に光二量化反応性を有する感光性基が化学的に導入されてなる成形体1をその上方に設置した後、コック9を開けて、真空ポンプ5によりベルジャー8内を真空にする。このときの真空度は 10^{-2} Torr以下であることが好ましい。ベルジャー内に酸素が残っていると後述する光照射の際に過酸化物が形成され、薄膜の形成が阻害されたりすることがあるので、一度窒素ガス等の光反応に対して不活性なガスでベルジャー内を置換した後、再度真空にすることが好ましい。さらに真空度が十分でないとき光感応性親水化処理剤が蒸発しにくかったりするので好ましくない。ヒーター4を加熱すると光感応性親水化処理剤は徐々に蒸発あるいは昇華し、ベルジャー内にその蒸気が充満する。もっとも、室温で本処理剤が昇華する場合には加熱する必要はない。

【0022】このようにして、成形体を光感応性親水化処理剤の蒸気内に存在せしめた後、成形体に窓7を通して光源6から紫外光線及び／又は可視光線を照射すると、成形体の光照射面に、光感応性親水化処理剤の感光性基と成形体表面の感光性基が反応して親水性基が導入され、表面の親水性を変化せしめることができる。本発明で用いられる窓は、光反応に必要な波長の光を透過する材質で形成されていることが必要である。又、この窓と光源の間には、集光レンズ10及び光学フィルター11等を適宜に配置することができる。

【0023】本発明は、また、本感光性基を導入した成形体表面上に適当なマスク、あるいは様々な遮光度の遮光スクリーンをかぶせてから光を照射したり光ビームの走査を行なうことによって、成形体上に親水部分と疎水部分からなるパターン形成、あるいは様々な親水性の濃淡模様が描かれた図形の描写を行うことが出来る。本発明の方法によって導入される親水基の濃度、したがっ

て親水性度は成形体表面での照射光の光量すなわち前記したように光度と照射時間との積によってほぼ一元的に制御することができる。したがって本法は、従来の光グラフト法におけるように多数の因子が複雑に関与し親水性を支配している系に比較して、一段と制御性能が優れ、極めて再現性の良い親水-疎水パターン、親水性濃淡図形等の模様を描写することができる。以下、本発明を参考例、実施例及び比較例によってさらに詳しく説明する。

【0024】

【実施例】

参考例 1

(無機系成形体表面への感光性基の導入) ガラス製の封管中に、9-アリルアントラセン2.2g、ジメチルクロロシラン1.9g、塩化白金酸・6水和物の10wt%イソプロピルアルコール溶液0.1mlを入れて脱気封管した後、100℃で6時間加熱した。開封後、反応液を濃縮し析出した固体をヘキサンより再結晶して9-アンスリルプロピルクロロジメチルシラン2.4gが得られた。さらに、得られた9-アンスリルプロピルクロロジメチルシランの1wt%トルエン溶液に、予め洗浄及び乾燥を施した1cm×2cmの大きさで厚さ4mmの石英板を1分間浸漬した後引き上げ、70℃で1時間熱処理して、表面にアンスリル基の結合した成形体を得られた。アンスリル基の結合していることは、成形体の可視-紫外吸収スペクトル測定より確認した。水に対する接触角を測定したところ90度であった。

【0025】参考例 2

(有機系成形体表面への感光性基の導入) シュートルカの方法(マクロモリキュール 8巻 8頁〜9頁 1975年)に従って合成した、1-(2-アンスリル)エチルメタクリレート0.2gとスチレン5.8g及びラジカル重合開始剤としてアゾビスイソブチロニトリル0.04gをベンゼン60ml中に溶解して脱気封管した後、60℃で12時間重合を行い、数平均分子量10万のポリマーが得られた。このポリマーを溶融成形して厚さ5mmで2cm角の板状成形体を得られた。本成形体表面にてアンスリル基が基体に結合していることは紫外-可視吸収スペクトル測定より確認した。この試料について水に対する接触角を測定したところ88度であった。

【0026】比較例 1

第1図の装置で、ボートに1gのアントラセンをとり、参考例1で調製した成形体を上方に設置し、ベルジャー内を窒素ガスで置換した後、真空ポンプによって 10^{-4} Torrの真空度に到達させた。ボートを150℃に加熱してアントラセンを昇華させながら、1kWの水銀ランプを光源として東芝(株)製L-39フィルターを通して、380nmより長波長の光を前記成形体に1分間光照射した。照射後の成形体の紫外-可視吸収スペクトルを測定したところアンスリル基の吸収(以後本吸収と

称する)は消失し、成形体表面のアンスリル基と昇華したアントラセンが反応していることが確かめられた。水に対する接触角を測定したところ89度で照射前とほとんど変化なかった。

【0027】比較例 2

ボートに何も入れなかった以外は比較例1と全く同じにして光を照射した。照射後の成形体の吸収スペクトルを測定したところ吸収にほとんど変化は認められなかった。照射後の成形体の水に対する接触角を測定したところ90度であり照射前と変化しなかった。

【0028】比較例 3

参考例2で調製した成形体を用いた以外は、比較例1と全く同じにして光を照射した。この被照射成形体の紫外-可視吸収スペクトルを測定したところ、本吸収は減少し、成形体表面のアンスリル基と昇華したアントラセンが反応していることが確かめられた。本被照射成形体の水に対する接触角を測定したところ86度の値が得られ、照射前とほとんど変化していないことが分かった。

【0029】比較例 4

参考例2で調製した成形体を用いた以外は、比較例2と全く同じにして光を照射した。この被照射成形体の紫外-可視吸収スペクトルを測定したところ、吸収にはほとんど変化が認められなかった。

【0030】実施例 1

ボートに3-(9-アンスリル)プロピオン酸1gをとり、加熱温度を190℃とした以外は比較例1と同じ条件で光を照射した。照射後の成形体の本吸収スペクトルは減少し、反応が起こりカルボキシル基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は60度に減少し親水性が変

【0031】実施例 2

ボートに9-アントラセンカルボン酸1gをとり、加熱温度を200℃とした以外は比較例1と同じ条件で光を照射した。照射後の成形体の本吸収スペクトルは減少し、反応が起こりカルボキシル基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は65度に減少し親水性が変

【0032】実施例 3

ボートに9-アントラセンメタノール1gをとり、加熱温度を160℃とした以外は比較例1と同じ条件で光を照射した。照射後の成形体の本吸収スペクトルは減少し、反応が起こりヒドロキシル基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は75度に減少し親水性が変

【0033】実施例 4

ボートに3-(9-アンスリル)プロピルアミン1gをとり、加熱温度を180℃とした以外は比較例1と同じ

条件で光を照射した。照射後の成形体の本吸収スペクトルは減少し、反応が起こりアミノ基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は55度に減少し親水性が変

【0034】実施例 5

参考例2で調製した成形体を用いた以外は、実施例1と全く同じにして光を照射した。この被照射成形体の紫外-可視吸収スペクトルを測定したところ、本吸収は減少しており、新にカルボキシル基の吸収が認められた。したがって本反応が起こりカルボキシル基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は65度に減少し親水性が変

【0035】実施例 6

参考例2で調製した成形体を用いた以外は、実施例4と全く同じにして光を照射した。この被照射成形体の紫外-可視吸収スペクトルを測定したところ、本吸収は減少しており、新にアミノ基の吸収が認められた。したがって本反応が起こりアミノ基の導入されたことが確かめられた。照射後の成形体の水に対する接触角を測定したところ、接触角は60度に減少し親水性が変

【0036】

【発明の効果】以上説明した本発明によれば、増感剤、光重合開始剤等の光反応系添加剤を配合・添加することなく、簡単なプロセスによって再現性良く種々の成形体表面の特定の位置に親水性基を導入したり、親水性の濃淡パターンを形成したりすることが出来るので、従来技術にては到達し得なかった高度の親水性光制御が可能となり、電子材料にて使用される各種基板の接着性の改良；オフセット印刷におけるマスター版の作製；人工骨、人工血管等の医用材料表面の生体適合性の改良；印刷性、ガス透過性を特殊デザインした包装用フィルム；透湿と汗吸水とを程よく調節する快適性衣料品；両性電解質型高分子膜等の多様な用途に好適に使用することができる。

【図面の簡単な説明】

【図1】図1は本発明の実施態様の一例として示した処理プロセス中の装置の概略図である。

【符号の説明】

- 1 成形体
- 2 ボート
- 3 光感応性親水化処理剤
- 4 ヒーター
- 5 真空ポンプ
- 6 光源
- 7 窓
- 8 ベルジャー
- 9 コック
- 10 集光レンズ

【図1】

